

STUDIES ON TARTRATE COMPLEXES

with special reference to the complex formation
with the copper(II) ion

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This dissertation summarizes the results from the following papers. They will be referred to by their Roman numerals.

- I. Johansson, L. and Larsson, R.
Circular Dichroism of Some Mono- and Binuclear Copper
(+)Tartrate Complexes in Aqueous Solution
Chemica Scripta 7, 67 (1975).
- II. Johansson, L.
The Complex Formation in Weakly Acid Solutions of
Copper(II) (+) Tartrate with Excess of Copper(II) ion
Studied by Potentiometric and Circular Dichroic Measure-
ments.
Chemica Scripta 7, 102 (1975).
- III. Johansson, L.
Complex Formation and Stereoselective Effects in the
Copper(II) *d*- and *dl*-Tartrate Systems in Acid and
Neutral Aqueous Solution.
Manuscript.
- IV. Hansson, E. and Johansson, L.
On the structure of a Polynuclear Copper(II) *d*-Tartrate
Complex in Neutral Aqueous Solution.
Manuscript.
- V. Johansson, L.
Complex Formation in the Copper(II) *meso*-Tartrate System
in Acid and Neutral Aqueous Solution.
Manuscript.
- VI. Johansson, L. and Nördén, B.
Circular Dichroism and the Configuration of Deprotonated
Tris-Tartrato Chromium(III) Complex.
Inorg. Chim. Acta 29, 189 (1978).

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INTRODUCTION

General properties of metal tartrate systems

The formation of complexes between the tartrate ion and various metal ions has been subject to extensive research practically as long as compleximetric investigations have been done. Even if not valid today the following quotation¹ is expressive, "It is hard to find a problem of complex chemistry which has been studied with as much stubbornness as the behaviour and structure of the various metallic tartrates and citrates". The reasons for this interest would to some extent be the early use of tartaric acid as a strong organic complexing agent in analytical chemistry, e.g. the presence of tartrate in Fehling's solution or at various surface conditioning processes², but the very rich variation of properties of tartrate complexes regarding stability, stoichiometry, dependency of pH and so on has certainly on its own merits contributed much to the interest in tartrate complexes.

The complex formation in acid and neutral copper tartrate solutions is the primary subject of this work, but many of the aspects discussed are common to the complex chemistry of metal tartrates on the whole. The early investigations on tartrate complexes were generally performed on alkaline solutions such as "tartar emetic" or Fehling's solution. The complex forming ability in such solutions is characterized by the formation of strong basic complexes. The formation of hydrolysed complexes is not, however, limited to the alkaline pH area, but such complexes are evidently formed together with normal complexes in neutral or weakly acid solutions. The appearance of hydrolysed complexes is for instance demonstrated by a decreasing pH when copper and tartrate solutions are mixed. The participation of the hydroxyl groups of the tartrate ion in the formation of the basic complexes was early surmised³ as was the importance of chelation, even if divergent ideas about the mode of chelation were current.

The question whether polynuclear - especially binuclear - complexes are formed in metal tartrate solutions has been discussed ever since the first investigations on tartrate complexes. Kahlenberg (1895) asserted that alkaline copper, lead, and antimony tartrate solutions contained dimeric units⁴ but was opposed by later investigators⁵. Quantitative studies of the equilibria in alkaline metal tartrate solutions are uncommon but the information from spectroscopic studies of such solutions, viz. vanadyl⁶ and copper⁷ dl-tartrate solutions, makes the existence of dimers seem probable. This existence is further supported by a number of crystal structure investigations⁸ of various alkaline metal tartrates in which discrete dimeric units are revealed.

The solubility of metal tartrates in non-alkaline solutions is generally rather low. Because of the fairly narrow concentration range accessible the description of experimental data from measurements in weakly acid or neutral solutions did not usually necessitate the introduction of polynuclear complexes even if in particular cases some facts indicated their presence⁹. However, the formation of a number of hydrolysed binuclear complexes, e.g. in uranyl¹⁰ and iron(III)¹¹ tartrate solutions, was demonstrated in acid solution. In 1966 Rajan and Martell showed that in acid copper tartrate solutions there was an equilibrium between the mononuclear complex and an unhydrolysed binuclear one. A similar equilibrium is believed to exist in acid nickel tartrate¹³ solutions.

The development of crystal structure determinations of metal tartrates has provided information that is to some extent applicable to tartrate complexes in solution. Most of these structure determinations concern alkaline metal tartrates⁸ of the general formula $(Me_I)_x Me_{II} C_4 H_4 O_6 \cdot y H_2 O$ (Me_I = alkali metal ion and Me_{II} = Cu^{2+} , Sb^{3+} , VO^{2+} , As^{3+}), but one of them deals with a normal tartrate¹⁴, viz. $CuC_4 H_4 O_6 \cdot 3 H_2 O$. All these structures contain tartrate-bridged dimeric units - as mentioned above the dimers appear in the case of alkaline tartrates as discrete units. It seems reasonable that the building principles of these dimers are applied when models of the binuclear complexes that appear

in alkaline as well as in acid metal tartrate solutions are outlined. The tartrate-bridged dimers will be described later in more detail in connection with a discussion of the binuclear complexes formed in acid copper tartrate solutions.

The structure determinations also show that the chelation is that normally found in complexes of α -hydroxy carboxylic acids, i.e. a five-membered chelate ring is formed by the coordination of one carboxyl oxygen and the adjacent hydroxyl oxygen to the same metal ion. Moreover, it is inferred that the formation of the basic tartrate solids takes place by the release of protons from the hydroxyl groups of the tartrate ion and not from coordinated water molecules. Considering that the acidity of the hydroxyl groups¹⁵ is comparable with that of water it could be expected that the basic complexes in acid and neutral aqueous solution also have released protons from these groups. Equilibrium measurements cannot determine if the protons come from the coordinated tartrate ions or water molecules. There is, however, a report from an examination of copper tartrate complexes in neutral solution with water molecules labelled with ¹⁸O that supports the idea of released hydroxyl protons¹⁶. Irrespective of the source of the basicity the notation of complexes adopted in paper III will be used in the following. Then a basic complex is written $\text{Cu}_p\text{T}_q\text{H}_r$ with a negative value of r and with T designating the "normal" tartrate ion $\text{C}_4\text{H}_4\text{O}_6^{2-}$. For simplicity the charge, $2(p-q)+r$, will also be omitted in the complex formulae.

The ligands

Tartrate molecules appear in three different isomers in which the asymmetric carbon atoms take the R,R -, S,S - or R,S -configurations. This results in the four ordinarily occurring types of tartrates which are generally denoted d - (R,R), l - (S,S), $meso$ - (R,S) and dl -tartrates, the latter being a racemic mixture of the two enantiomeric forms R,R and S,S . As the d - and l -tartrates separately consist of enantiomeric d - and l -tartrate molecules, they are equivalent as long as properties not depending on the asymmetry are concerned. However, a

dl-compound (racemate) differs generally in some aspect from the corresponding *d*- or *l*-analogues, and at its formation stereoselective effects may be discerned. For instance a *dl*-compound may be built up either from subunits containing both *d*- and *l*-enantiomers or from equal amounts of pure *d*- and *l*-subunits.

In order to understand the possibilities for coordination and the differences between various tartrates the information concerning the geometry of the ligand attained from crystal structure determinations is very valuable. The consistency as to the geometry and conformation of each kind of tartrate molecule that is obtained from the structure determinations of the acids as well as their alkali metal salts¹⁷⁻²³, makes it probable that the general shapes of the tartrate isomers are essentially determined by internal properties. The reproductions of the *d*- and *meso*-tartrate ions in fig. 1 and 2, which show the configurations and conformations and which are drawn with the guidance of data from the solid state, can thus be expected to represent the situation in solution.

The *d*-tartrate ion is characterized by three approximate planes. Two planes are defined by each carboxyl group with adjacent carbon and α -hydroxyl oxygen atoms. This coplanarity that is typical of α -hydroxocarboxylates²⁴, offers a distance between the hydroxyl and adjacent carboxyl oxygen atoms appropriate for the formation of a five-membered chelate ring. The third plane is made up from the four carbon atoms. As is demonstrated in fig. 2a this latter coplanarity is equivalent to a staggered conformation and an opposite position of the carboxyl groups.

The *meso*-tartrate structures examined do not retain the plane of carbon atoms. The conformation is still a staggered one but the carboxyl groups are placed in an adjacent position (fig. 2b). Such a tartrate molecule is asymmetric, and *meso*-tartrates, which are optically inactive, are racemic mixtures of the two enantiomeric conformations.

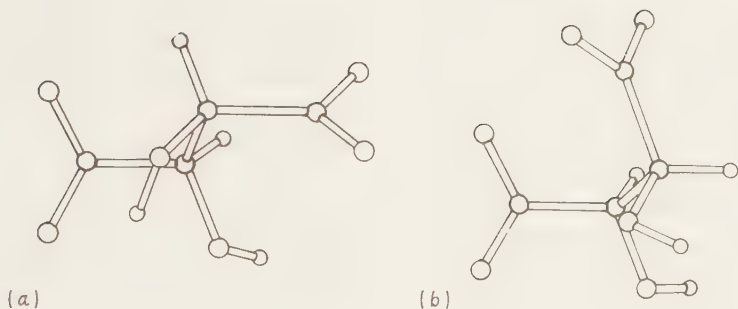


Fig. 1. Structural models of (a) the *d*-tartrate ion and (b) the *meso*-tartrate ion. The *meso*-tartrate ion is represented by one of its enantiomeric forms.

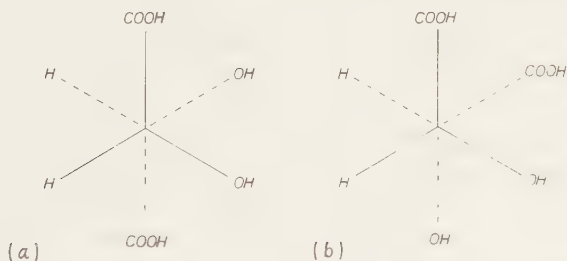


Fig. 2. Conformations of (a) *d*-tartrates and (b) *meso*-tartrates.

The conformations of the tartrate molecules seem to be determined by the distances between oxygen atoms situated at different halves of the tartrate molecule.²² Provided that all steric parameters are unchanged except those depending on a rotation around the central carbon-carbon axis, all conformations except those experimentally confirmed will result in oxygen-oxygen contacts closer than two van der Waals radii. For a free, uncoordinated *meso*-tartrate ion in solution with the same conformation as in the solid phase the proximity of two negative charges must cause coulombic repulsions between these charges, any other conformation will induce contact repulsions between oxygen atoms. Whatever conformation the free *meso*-tartrate ion may take in solution it will accordingly be expected to contain

a greater amount of repulsive energy than the *d*- and *l*-tartrate ions.

Presentation of the reviewed papers

The papers on tartrate complexes which are discussed in this work are confined to copper(II) tartrate complexes formed in acid and neutral aqueous solution except one paper that deals with the behaviour of a chromium(III) tartrate complex over a wider pH-range.

Copper and chromium *d*-tartrate solutions exhibit circular dichroism in the ligand field absorption bands - a fact that has been known since Cotton²⁵ for the first time demonstrated the existence of the phenomenon in solution. Measurement of circular dichroism is the main method in paper I and is used together with potentiometric methods in paper II and VI. The work described in paper I and II originally aimed at the determination of the CD-spectra of mono-copper and mono-tartrate complexes in order to correlate circular dichroism to the formation of chelates. With a growing understanding of the complexity of the copper tartrate system the purpose of the investigation was extended to the characterization of all species formed and their spectra.

Paper III describes a potentiometric investigation of acid and neutral solution of copper *d*- and *dl*-tartrate. The main purpose of this investigation was to examine if there are stereoselective effects in the complex formation of the copper *dl*-tartrate system in this pH-range, but it also aimed at a further elucidation of some other unsettled aspects of the complex formation such as the degree of polymerisation, complexes formed in neutral solution and the existence of some other dubious complexes.

There have been very few investigations on the copper *meso*-tartrate system leading to the specification of the complexes formed and their stabilities. The different configuration of the *meso*-tartrate ion should be expected to cause some differences in complex formation compared to the *d*- and *dl*-systems,

e.g. in the ability to form binuclear complexes. Paper V presents a study of the copper *meso*-tartrate system under the same experimental conditions as those valid in the study of paper III.

Neutralization of copper tartrate solutions shows the existence of an equivalence point²⁶ when 1.25 mol OH⁻/mol Cu(II) is added, indicating the formation of a complex that is at least tetranuclear. Such a neutralized solution with *d*-tartrate could be made sufficiently concentrated for a large angle X-ray investigation which is described in paper IV.

The possibility of deprotonation of the hydroxyl groups upon coordination implies a substantial dependence on pH for tartrate complexes. The study of the tris(*d*-tartrato)chromium(III) complex in paper VI may be seen as an illustration of this matter, but it also demonstrates another instance of stereoselective complex formation in the coordination chemistry of tartrates.

EXPERIMENTAL METHODS

Equilibrium measurements on copper tartrate solutions

Solutions

All measurements of this kind have been performed in the acid and neutral pH-range. Solutions used for measurement have been prepared from copper perchlorate, sodium tartrate or tartaric acid, and sodium hydroxide. In order to reduce the effects of a variable medium a formal ionic strength equal to one mol.dm⁻³ has been maintained by the addition of sodium perchlorate. For the same reason the range of concentrations of the reactants has been restricted - the highest tartrate concentration amounts to about 150 mM. The fairly low solubility of copper tartrate in acid solution is another limiting factor as regards concentration. It has been possible to perform measurements on equimolar solutions with a total concentration equal to 20 mM but

these solutions are supersaturated. The potentiometric measurements were carried out as titrations. In each titration as well as each spectrophotometric measurement series two concentration variables - the total concentration of copper and hydrogen ion in paper I, of copper and tartrate ion in papers III and V, and of tartrate ion and pH in paper II - were kept constant while the remaining one was varied.

Potentiometric measurements

The potentiometric measurements on the copper tartrate systems (II, III and V) aimed at the collection of data for an analysis of the complex equilibria and the calculation of stability constants. A copper amalgam electrode was used together with a glass electrode in all the potentiometric measurements. The potential of each electrode was measured against an Ag,AgCl reference electrode. The disproportionation reaction $\text{Cu(II)} + \text{Cu(am)} \rightleftharpoons 2 \text{Cu(I)}$ makes the amalgam electrode less suitable for measurements at very low total concentrations of copper(II). Here the electrode has been used at copper concentrations as low as 1 mM.

Protolysis constants of the tartaric acids used in the calculations were determined potentiometrically in separate measurements. The temperature in the potentiometric measurements was kept at 25°C except for those of paper II which were performed at 20°C.

Spectrophotometric measurements

The spectrophotometric measurements (paper I and II) consist of the recording of circular dichroism and absorption spectra in the wavelength region of the *d-d* transitions of the copper(II) ion. The available wavelength region of the dichrograph limited, however, the CD measurements to wavelengths shorter than 800 nm. As the recording of spectra originally aimed at the determination of the individual spectra of the particular species by the use of stability constants taken from the literature, the

spectrophotometric measurements were performed at a corresponding temperature equal to 20°C.

Solution X-ray investigation

The sharp appearance of an equivalence point in the titration curve upon neutralization of an equimolar solution of copper(II) and *d*-tartrate ions makes it probable that such a neutralized solution is dominated by one complex. From the potentiometric data of paper III the stoichiometric composition of the species formed can be ascertained but it can not be exclusively settled if the complex is tetra- or octanuclear or if both of them exist. However, the existence of a single complex is supported by the recordings of circular dichroism and absorption spectra of neutralized copper tartrate solutions in paper IV which show that Beer's law is valid over a wide concentration range.

The large angle X-ray investigation on a concentrated (1.75 M) neutralized copper *d*-tartrate solution was performed for the purpose of getting further information in order to decide upon the nuclearity of the complex. The relatively low atomic number of copper necessitates a high concentration of the solution, which is possible in the case of copper *d*-tartrate - the limiting factor seems not to be the solubility but rather a beginning reduction of copper(II) to copper(I)oxide. In the case of copper *dl*-tartrate, the neutralized solution of which also contains polynuclear complexes, a similar investigation is thwarted by the much lower solubility.

Chromium tartrate measurements

The variation of the circular dichroism of chromium(III) solutions with a large excess of *d*-tartrate was studied when pH was changed from about 4 to 12. The total concentration of tartrate was equal to one mol·dm⁻³ and this excess of tartrate constituted its own constant ionic medium. The average number of protons released from the chromium tartrate complexes was

determined from the measurements of pH. The method gives a reliable assessment of this number down to pH about 5, but at this pH the beginning protonation of the tartrate(2-) ion makes the measurement of pH less sensitive to changes in the protonation of the complexes. This formation of hydrogen tartrate species may also effect the constancy of the ionic medium.

CALCULATIONS AND RESULTS

Stability constants and spectra

The occurrence of normal as well as acid and basic complexes implies that the systems should be treated as mixed systems made up from three components, copper(II), tartrate(2-) and hydrogen ions. The application of graphical methods in the calculations on such systems, which are further complicated by the appearance of polynuclear complexes, is very tedious and demands a large amount of data. The experimental conditions allow a complete graphical treatment of data in one case only - the potentiometric measurements at constant pH (paper II). However, all stability constants presented are the result of numerical methods which are based upon the principle of least-squares. These methods do not explicitly give an exclusive list of complexes present in the system under calculation, but in an analysis free from presumptions the existence of a great many conceivable complexes has to be checked. Then a "best" set of complexes has to be chosen on the basis of the results obtained in the calculations. This choice is not directed only from the goodness of fit - which can be made almost perfect if a sufficiently complicated model is chosen - but is combined with a general aim of finding a description as simple as possible, i.e. complexes of low abundance and with constants of low statistical significance have been omitted, sometimes at the sacrifice of the goodness of fit.

Potentiometric data

In potentiometric measurements the measured quantity, the emf, is expressed as a function of the concentration of one of the participants of the complex formation, and this concentration is related to the total concentrations of the reactants via expressions that contain the unknown stability constants. The absence of intensive factors in these expressions makes the mathematical treatment of potentiometric data safer than is usual in the case of data from other kinds of measurements, for instance spectrophotometric data. However, the consequences of systematic errors inherent in the potentiometric method may be serious. Variations of the ionic medium affect the constancy of the stability constants as in all measurements on equilibria but to this must be added the effect on the activity coefficient of the species involved in the emf expression as well as the appearance of liquid junction potentials. Unfortunately, these two effects cannot be experimentally separated and it is hard to formulate a theoretical basis suitable for a quantitative correction. As a consequence the methods used for correction have to be of empirical character founded on separate measurements.

It was observed in the potentiometric measurements in paper II that E° varied in a linear way with the concentration of Cu^{2+} when copper perchlorate replaced sodium perchlorate in a solution of constant formal ionic strength. The deviation from a constant value of E° was rather small - about $-6 \text{ mV} \cdot \text{M}^{-1}$ - but is of some importance in the measurements of paper II where the copper concentration is rather high. The continued examinations for appropriate correction terms indicate, however, that the corresponding replacement of sodium perchlorate with sodium tartrate - still maintaining a constant formal ionic strength - should cause a much greater deviation of E° - estimated to about $58 \text{ mV} \cdot \text{M}^{-1}$. In some of the measurement series of paper III and V the tartrate concentration is so high that this deviation cannot to be neglected.

In paper III the above observations are extended to the hypothesis that every electrolyte in the complex solution potentially

Table 1. Stability constants and mean proton numbers $\bar{n}$ of complexes formed in copper(II) *d*-tartrate solution with a copper to tartrate ratio equal to and greater than one. Measurements are performed at pH = 4.40, $t = 20^\circ\text{C}$ and ionic strength 1.00 M with NaClO₄ as neutral salt. Stated errors are equal to three standard deviations. The constants are conditional and refer to the total formation of complexes with a copper to tartrate ratio given by the formula Cu_pT_q.

	Potentiometric measurements	CD-measurements	$\bar{n}$
$\beta_{11}^- / \text{M}^{-1}$		$(5.7 \pm 0.8) \cdot 10^2$	-0.1 ± 0.3
$\beta_{21}^- / \text{M}^{-2}$		$(3.5 \pm 0.7) \cdot 10^4$	-1.0 ± 0.4
$\beta_{31}^- / \text{M}^{-3}$	$(1.9 \pm 0.2) \cdot 10^6$		
$\beta_{22}^- / \text{M}^{-3}$	$(1.32 \pm 0.09) \cdot 10^9$	$(7.7 \pm 1.3) \cdot 10^8$	-0.83 ± 0.15
$\beta_{64}^- / \text{M}^{-9}$	$(1.90 \pm 0.10) \cdot 10^{25}$	$(9.8 \pm 1.4) \cdot 10^{24}$	-5.8 ± 0.2
$\beta_{84}^- / \text{M}^{-11}$	$(9.2 \pm 0.6) \cdot 10^{28}$	$(9.5 \pm 1.2) \cdot 10^{28}$	-7.74 ± 0.12
$\beta_{104}^- / \text{M}^{-13}$	$(1.9 \pm 0.2) \cdot 10^{31}$		

contributes to the deviation from a constant value of $\bar{n}^0$ and that this deviation can be treated within a fairly wide concentration range as a sum of linear terms, one for each electrolyte. However, the concentrations used and the assumption that the linear coefficients of the complex electrolytes are small - partly a consequence of the linking of the coefficients to electrolytes and not to the particular ions - would justify the omission of the unknown contributions of the complexes.

For the calculations on the measurements performed at constant pH in paper II the Letagrop program ETITRE²⁷ was used. The data were originally evaluated by a graphical method and the obtained set of complexes was used as a basis for the numerical calculations, but the presence of some additional complexes was tested too. Equal weights were given to all experimental points. The resulting stability constants, which are given in table 1, will necessarily be of conditional character and valid only at

the given pH of 4.40. However, the average number of released protons, also shown in table 1, give some information of the proton stoichiometry of the complexes.

In the measurements of paper III and V two emfs are measured simultaneously, which gives rise to a correlation between the experimental errors of the two measurements. Moreover, there are steep increases of the emfs in a certain pH-range resulting in larger experimental errors. This actualized the question of a more proper weighting. However, the correlations between the emfs cannot be directly estimated from the experimental data, so they are calculated by means of the analytical emf expressions and the stoichiometric relations. A more detailed account is given in paper III. For the calculations on the data of paper III and V the general minimizing Fortran procedure STEPIT²⁸ was used, completed with the necessary procedures for tackling the present problem.

The stability constants calculated from the potentiometric measurements on the systems of copper *d*-tartrate, copper *dl*-tartrate (paper III) and copper *meso*-tartrate (paper V) are collected in table 2. No definite presumptions as to the number or composition of the complexes were given in these calculations, but the final sets of complexes have been obtained after the testing of many plausible complexes. For the description of the systems a rather large number of complexes, many of which are present in the same concentration range, is required. Under such conditions it may be difficult to decide on smaller details of the models so complexes of low maximum concentration are excluded.

Spectrophotometric data

The measured property in the spectrophotometric measurements is normally a function of the concentrations of more than one species. Each of these species contributes with a term that contains an intensive factor - in this case a CD-coefficient or an absorptivity. If these intensive factors cannot be determined separately, the complete evaluation of data implies the

Table 2. Stability constants of complexes $\text{Cu}_p\text{T}_q\text{H}_r$ formed in acid and neutral copper d^- , $d\ell^-$ and $meso$ -tartrate solutions calculated from data of potentiometric measurements at 25°C and ionic strength 1.00 M with NaClO_4 as neutral salt. Stated errors are equal to three standard deviations.

p q r	d-tartrate	d ℓ -tartrate	d ℓ -complexes ^a	meso-tartrate	
1 1 1	$(3.84 \pm 0.14) \cdot 10^5$	$(3.70 \pm 0.15) \cdot 10^5$		$(1.53 \pm 0.03) \cdot 10^6$	M ⁻²
1 1 0	$(4.3 \pm 0.3) \cdot 10^2$	$(4.5 \pm 0.3) \cdot 10^2$		$(1.41 \pm 0.05) \cdot 10^3$	M ⁻¹
1 2 0	$(2.44 \pm 0.14) \cdot 10^4$	$(2.36 \pm 0.11) \cdot 10^4$	$(4.6 \pm 0.5) \cdot 10^4$	$(2.05 \pm 0.06) \cdot 10^5$	M ⁻²
2 2 0	$(4.00 \pm 0.13) \cdot 10^8$	$(2.04 \pm 0.08) \cdot 10^8$	$(0.2 \pm 0.4) \cdot 10^8$	$(3.3 \pm 0.3) \cdot 10^8$	M ⁻³
2 2 -1	$(1.60 \pm 0.08) \cdot 10^4$	$(0.98 \pm 0.10) \cdot 10^4$	$(0.7 \pm 0.4) \cdot 10^4$		M ⁻²
2 2 -2	$(4.4 \pm 0.2) \cdot 10^{-1}$	$(3.0 \pm 0.4) \cdot 10^{-1}$	$(3.1 \pm 1.6) \cdot 10^{-1}$		M ⁻¹
4 3 -4		$(3.4 \pm 0.5) \cdot 10^{-1}$			M ⁻²
4 3 -5		$(1.42 \pm 0.14) \cdot 10^{-5}$			M ⁻¹
5 4 -5				$(1.09 \pm 0.16) \cdot 10^4$	M ⁻³
5 4 -6				1.36 ± 0.08	M ⁻²
6 4 -7	$(3.0 \pm 0.3) \cdot 10^{-6}$			$(1.64 \pm 0.13) \cdot 10^{-1}$	M ⁻²
6 5 -7		$(1.1 \pm 0.2) \cdot 10^{-2}$			M ⁻³
8 6 -10	$(4.2 \pm 0.5) \cdot 10^{-8}$				M ⁻³

^a Calculated from eq. 16 in paper III

calculation of the intensive factor and the stability constant of each complex. The possibility to do this in a satisfactory way is influenced by a number of properties, the importance of which may vary from system to system,

1. First of all there has to be an appreciable difference in the magnitudes of the intensive factors of different complexes so that any change in the measured property can be observed.
2. If a complex is very strong the intensive factor may be well determined but the stability constant would be uncertain.
3. On the other hand if a complex is weak compared to the others and never reaches a high concentration, the product of the stability constant and the intensive factor may possibly be calculated with acceptable statistical significance but it would be hard to determine their individual values.
4. If several complexes are present in the same concentration range the large number of unknown parameters in the mathematical expression may further complicate the problem of correlation.

The first of the above conditions is mostly well met in the CD-measurements - there is a considerable change in the circular dichroism as the concentration variables are changed. However, several complexes are normally present at the same time and some of them - especially the mononuclear ones - at low concentrations in areas with predominant binuclear complexes, which are fairly strong. This implies that problems of all the remaining kinds may be expected to interfere in a calculation aiming at a simultaneous determination of the CD-coefficients as well as the stability constants. The possibility of a satisfactory evaluation of data is of course also influenced by the appearance of possible systematic errors. Besides those caused by changes in the ionic medium instrumental inadequacies may, though fairly well controlled, seriously disturb the interpretation of data because of a more delicate mathematical situation.

With consideration of the above it has been necessary to perform the calculations on the spectrophotometric data with a lower degree of completeness - in the first place regarding the choice

of the number of complexes to be tested. The sets of complexes have been taken from other investigations and the additional test of other complexes has been restricted to a small number of some particular interest.

In the calculations on the CD-data of paper I - from measurements on solutions with equal amounts and excess of tartrate in relation to copper - a set of complexes taken from Bottari *et al.*²⁹ was applied. Predetermined stability constants of some of the complexes were also used. The results of these calculations, stability constants and spectra, are given in paper I.

The potentiometric measurements on copper *d*-tartrate described in paper III gave a description of the system that differed from that of Bottari in some details. The calculations on the CD-data of paper I were repeated with consideration to the changes. Spectra were calculated by the use of the potentiometrically determined stability constants but an attempt without presumptions on the values of the stability constants was also made. These latter calculations seem to be susceptible to difficulties of the kind mentioned on page 19 under paragraph 2, *i.e.* the complexity is somewhat too strong for a safe evaluation of the stability constants. However, the obtained constants are of the same order of magnitude as those potentiometrically determined but the statistical significance of their values is low. These repeated calculations are accounted for and their results presented in the appendix.

The main difference between the two applied models consists of the exchange of the complex Cu_2T_3 in the original paper against the complex $\text{Cu}_2\text{T}_2\text{H}_{-1}$. The exchange does not affect the general shape of the spectra of the predominant complexes very much. However, the CD-spectrum of CuT in fig. 1 in the appendix has a magnitude that agrees better with the spectrum of CuT calculated from the measurements at constant pH in paper II (fig. 3). It may also be noted that the presence of polynuclear complexes which is made clear in the examinations of paper III, interferes at the separate determination of the spectrum of $\text{Cu}_2\text{T}_2\text{H}_{-2}$

presented in fig. 4, paper I. This spectrum is accordingly better represented by fig. 3 in paper I or fig. 1 in the appendix.

The stability constants from the calculation on CD-data from the measurements of paper II on solutions with excess of copper and at constant pH are given in table 1 together with the constants from the corresponding potentiometric measurements. The spectra are reproduced in fig. 3 of paper II. With the exception of a couple of minor departures, which are evident from table 1, these calculations are founded on the set of complexes obtained from the potentiometric measurements, but in the calculations no presumptions on the values of the constants are made. The conditions for a more independent treatment of data are more favourable in this case as the complex formation can be regarded as taking place between only two components.

The data from the absorption measurements have in no case been used for the evaluation of stability constants. For the calculations of the absorption spectra of the complexes the same stability constants were used as for the calculation of the CD-spectra.

The calculations on the spectrophotometric data were performed by the use of the Letagrop program SPEFO³⁰, slightly modified to allow for negative CD-values.

Interpretation of solution X-ray scattering data

Scattering data from X-ray irradiation of liquid solutions give, through the radial distribution curve, information on atomic distances. The knowledge of distances alone does not allow the derivation of an exclusive structure of a complex containing many atoms. The aim must be limited to find a plausible structure which describes the scattering data. For this purpose information has to be taken from other sources. In this case the building principles of the structure of the octanuclear complex, $\text{Cu}_8\text{T}_6\text{H}_{10}$, has been conjectured on the basis of findings from the potentiometric and the circular dichroism measurements (paper I, III and IV), and the geometrical parameters of the

integral parts of the structure have mainly been taken from the crystal structure of $\text{Cu } d\text{-C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$.¹⁴ Tartrate-bridged dimeric units of the kind occurring in the latter compound have been joined in a row by two copper ions via the hydroxyl oxygens of the tartrate ions. All hydroxyl protons are released except one at each of the outermost tartrate ions. A sketch of the proposed structure is shown in fig. 4 in paper IV.

DISCUSSION

Complex formation of the copper tartrate systems

General features

In acid solutions when pH is between about two and four and at fairly equal amounts of copper and tartrate all the copper tartrate systems develop an equilibrium between the mononuclear complexes CuTH and CuT and a binuclear complex Cu_2T_2 even if the latter is somewhat less important in the *meso*-tartrate system. In the *d*- and *dl*-tartrate systems the binuclear complex starts hydrolysing into $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and $\text{Cu}_2\text{T}_2\text{H}_{-2}$ when pH approaches and exceeds four, while these hydrolysed complexes are negligible in the case of *meso*-tartrate. In all the systems a polymerisation starts at pH larger than four, the course of which differs to some extent in the various systems but which ends in all the three cases with a rapid change of pH to about eight when up to 1.25 mol $\text{OH}^-/\text{mol Cu(II)}$ is added.

With excess of tartrate the binuclear complexes mentioned are still important but the second mononuclear complex CuT_2 is also formed. For the description of the present data the introduction of the third mononuclear complex is not necessary even if its existence cannot be excluded at the highest tartrate concentrations used. It must, however, be pointed out that any quantitative interpretation of the experimental data at high tartrate concentrations may be doubtful because of changes of the medium. As may be seen from the analysis of the emf correction in paper III, it is evident that the exchange of large

amounts of sodium perchlorate against sodium tartrate will have serious effects.

The copper d-tartrate system

Among the copper tartrate systems studied in this work only the d-tartrate system has been subject to both potentiometric and spectrophotometric methods. The CD-data of paper I are derived from concentration ranges that are in parts covered by the potentiometric measurements of paper III. Even if the attempt to make an independent calculation of the stability constants from the CD-data (appendix) shows that these data alone do not allow the determination of highly significant constants, it is evident that both types of data can be described by the same set of complexes.

In the original description of the CD-data the complex Cu_2T_3 plays a pronounced role. The introduction of the complex in the calculations on the potentiometric data of paper III showed that the presence of the complex was not necessary. The repeated calculations on the CD-data showed that an exchange of the complex against $\text{Cu}_2\text{T}_2\text{H}_{-1}$ gave a slightly better description of the data. Even if the existence of Cu_2T_3 cannot be excluded it is evident that the magnitude of its constant as presented in paper I is far too large.

Potentiometric titration curves (paper III) as well as the applicability of Beer's law (paper IV) indicate that one complex is quantitatively formed in copper d-tartrate solutions neutralized with 1.25 mol OH^- /mol Cu(II). The calculations on the potentiometric data show that the complex has the composition $\text{Cu}:\text{T}:\text{H} = 4:3:-5$ and that, on the assumption that only one complex is formed, this complex should be $\text{Cu}_8\text{T}_6\text{H}_{-10}$. The possibility of producing a structural model that is consistent with the liquid diffraction data (paper IV), also supports the formation of the octanuclear complex. The characterization of additional complexes formed in the region $-1 > \text{C}_\text{H}/\text{C}_\text{M} > -1.25$ is uncertain. It is interesting, however, that the complex that

fits the data best - $\text{Cu}_6\text{T}_4\text{H}_{-7}$ - can be regarded as a natural intermediate part in the growth of the proposed structure of $\text{Cu}_8\text{T}_6\text{H}_{-10}$.

The measurements at constant pH in paper II include concentration areas with excess of copper. In these areas both potentiometric and CD-data are best described with complexes that contain four tartrate ions and a various number of copper ions. The calculated mean proton numbers reveal that despite the moderate pH, nearly two protons per tartrate(2-) ion are lost. Consequently the predominating complex in this area should be $\text{Cu}_8\text{T}_4\text{H}_{-8}$. The potentiometric measurements indicate that at the highest copper concentrations ($C_M \approx 100$ mM) complexes with more than two copper ions per tartrate ion are formed while the calculations on CD-data do not demand the introduction of such complexes. The potentiometric data from this concentration range are necessarily subject to serious systematic errors but taking this into consideration it still seems probable that complexes with more than two copper ions per tartrate ion are formed. However, the composition of complexes of this kind proposed in paper II have to be considered as tentative.

The copper dl-tartrate system

Complexes formed in the d-tartrate system should of course appear in the dl-system together with their l-tartrate analogues. Furthermore complexes that contain both d- and l-tartrate ions, here denominated dl-complexes, can also be present. The formation of several different complexes with the formula $\text{Cu}_p\text{T}_q\text{H}_r$ in the dl-system but with various proportions of d- and l-tartrate ions is in table 2 jointly represented by a stability constant, β_{pqr} . At a comparison of the constants of the d- and dl-tartrate systems consideration has to be taken of the fact that the treatment of the d- and l-tartrate ions of the dl-system as one and the same ligand causes a difference of the standard states of the two systems. Eqs. 15 and 16 in paper III show the relation between such a total constant of the dl-system and the constants of the particular species summarized in this

constant but referring to the normal standard state. These equations make it possible in simple cases to calculate the constant of a dl -complex usable for a direct comparison with the corresponding constant of the pure d -complex. Such constants are presented in the fourth column of table 2.

As long as the complexes contain only one tartrate ion the question of stereoselectivity is inappropriate and the constants of the d - and dl -systems are expected to be equal. With due consideration to the errors it is seen from table 2 that this is the case.

The formation of a dl -complex $Cu_p(d-T)_{q-n}(l-T)_n$ is statistically favoured by a factor $\binom{q}{n}^{31}$. Considering this factor it turns out that the second mononuclear complexes $Cu(d-T)_2$, $Cu(l-T)_2$ and $Cu(d-T)(l-T)$ are formed in the proportions that are statistically expected if no other stereoselective effects are active.

The formation of the binuclear complex Cu_2T_2 is practically stereospecific in favour of the pure dd - and ll -complexes. In the case of the complexes $Cu_2T_2H_{-1}$ and $Cu_2T_2H_{-2}$ the formation of dd - and ll -complexes is still promoted but increasing amounts of the dl -complexes are formed. The influence of the continued polymerisation makes, however, the values of corresponding constants rather uncertain and dependent on small changes in the chosen models. Therefore a statement about the formation of these dl -complexes should be limited to the declaration that at least the dl -complex of $Cu_2T_2H_{-2}$ is formed in appreciable amounts.

The formation of d - and l -complexes of $Cu_8T_6H_{-10}$ is surpassed by the strong dl -complex $Cu_4T_3H_{-5}$. The formation of less hydrolyzed polynuclear complexes - with $-1 > r/p > -1.25$ - is also more pronounced than in the d -tartrate system. Their characterization is necessarily uncertain - the tentatively proposed complexes $Cu_4T_3H_{-4}$ and $Cu_6T_5H_{-7}$ represent the simplest description.

Table 3. Equilibrium constants of some corresponding copper *d*- and *meso*-tartrate reactions.

Reaction	K/M^{-1} (<i>d</i>)	K/M^{-1} (<i>meso</i>)	K_{meso}/K_d	no.
$T^{2-} + H^+ \rightleftharpoons HT^-$	$4.90 \cdot 10^3$	$13.3 \cdot 10^3$	2.71	(1)
$HT^- + H^+ \rightleftharpoons H_2T$	$5.57 \cdot 10^2$	$7.59 \cdot 10^2$	1.36	(2)
$Cu^{2+} + T^{2-} \rightleftharpoons CuT$	$4.3 \cdot 10^2$	$14.1 \cdot 10^2$	3.31	(3)
$CuT + H^+ \rightleftharpoons CuTH^+$	$9.0 \cdot 10^2$	$10.9 \cdot 10^2$	1.20	(4)
$HT^- + Cu^{2+} \rightleftharpoons CuTH^+$	$0.78 \cdot 10^2$	$1.15 \cdot 10^2$	1.47	(5)
$CuT + T^{2-} \rightleftharpoons CuT_2^{2-}$	$0.57 \cdot 10^2$	$1.45 \cdot 10^2$	2.54	(6)
$CuT_2^{2-} + Cu^{2+} \rightleftharpoons Cu_2T_2$	$1.64 \cdot 10^4$	$0.16 \cdot 10^4$	0.10	(7)
$2CuT \rightleftharpoons Cu_2T_2$	$2.20 \cdot 10^3$	$0.16 \cdot 10^3$	0.08	(8)

The copper *meso*-tartrate system

The mononuclear copper *meso*-tartrate complexes are stronger than corresponding *d*-tartrate complexes. The same is true for the hydrogen *meso*-tartrate complexes. A comparison of the equilibrium constants of table 3 shows that the constant of a reaction in which an uncoordinated *meso*-tartrate(2-) ion is involved is about three times larger than the constant of the corresponding *d*-tartrate reaction (reactions no. 1, 3, and 6 in table 3). When attaching a second ion to the tartrate ion the constants of the *meso*-tartrate reactions are still larger but the ratio is now only one to one and a half (reactions no. 2, 4, and 5).

The stability constant of the dimeric *meso*-tartrate complex is about the same size as that of the corresponding *d*-tartrate complex. A comparison of the dimerization reactions (no. 8 in table 3) shows, however, that the tendency of dimerization is much weaker in the *meso*-tartrate system.

The preparation of solid phases with the composition $\text{Na}_3\text{Cu}_4\text{T}_3\text{H}_{-5} \cdot x\text{H}_2\text{O}$ has been reported³² for *meso*-tartrate as well as for *d*- and *dl*-tartrate. The formation of a copper *meso*-tartrate complex corresponding to this composition cannot be established - nor excluded - from the potentiometric data of paper V. The rise of pH occurs a little earlier in the *meso*-tartrate system and is caused by an almost quantitative formation of a complex $\text{Cu}_5\text{T}_4\text{H}_{-6}$. As in the *d*- and *dl*-tartrate systems there are also formed less hydrolyzed polynuclear complexes, the characterization of which is associated with the same kind of difficulties.

Structural aspects of the copper tartrate complexes

Mononuclear complexes

The magnitudes of the stepwise formation constants of the first and second mononuclear copper tartrate complexes support the idea that these complexes are chelated in aqueous solution. Even if a comparison with the monobasic ions in table 4 must not be overdone both K_1 and K_2 are larger than corresponding values for the glycolate ion which is supposed to form chelates with copper.⁹ When regarding the value of K_1 of the singly-charged hydrogen *d*-tartrate ion it should be noted that the *d*-tartaric acid is about seventy times as strong as acetic acid and about ten times as strong as glycolic acid.

The recalculation of CD-spectra in the appendix gave rise to a more reliable CD-spectrum of $\text{Cu}(d\text{-T})$ and it was shown at the same time that though a reliable spectrum of $\text{Cu}(d\text{-T})_2$ could not be obtained, the circular dichroism of CuT_2 is much less than that of CuT . The negative sign and the wavelength of the minimum of CuT are consistent with CD-spectra of copper (+)-lactate.³⁴ The fairly large circular dichroism of CuT - about six times larger than that estimated for the first copper lactate complex - also supports a chelated complex.

Table 4. Stepwise formation constants of some copper carboxylates and protolysis constants of corresponding carboxylic acids.

	$\log K_1$	$\log K_2$	pK_a	Ref.
CH_3COO^-	1.71	1.00	4.57	33
$\text{CH}_2(\text{OH})\text{COO}^-$	2.31	1.34	3.62	33
$\text{CH}_3\text{CH}_2(\text{OH})\text{COO}^-$	2.45	1.49	3.64	33
$d\text{-TH}^-$	1.89		2.74	III
$d\text{-T}^{2-}$	2.63	1.75	3.69	III
$meso\text{-TH}^-$	2.06		2.88	V
$meso\text{-T}^{2-}$	3.15	2.16	4.12	V

The great theoretical and mathematical difficulties of the quantitative as well as qualitative correlation of circular dichroism of metal complexes to structural properties usually limits the use of the CD-measurements to empirical comparisons of related compounds. Unfortunately there are very few reports on the circular dichroism of the copper complexes with optically active α -hydroxocarboxylates. CD-measurements on copper complexes with *L*- α -amino acids show, however, that the addition of a second optically active chelating ligand normally more than doubles the circular dichroism.³⁵ An estimation of the circular dichroism of the copper lactate complexes also shows that the CD increases by a factor of two.

The decrease of the circular dichroism when the second tartrate ligand is coordinated could perhaps be explained by the formation of a *cis*-complex, *i.e.* a complex with the two carboxyl oxygens in the *cis*-position, in which the CD-effects of two chelates cancel each other.³⁶ The formation of an electrostatically less favourable *cis*-isomer of the *dd*-complex should,

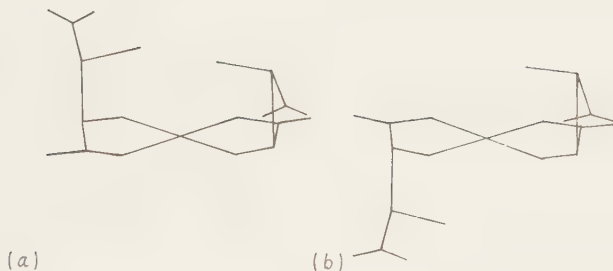


Fig. 3. Sketches illustrating the effects of (a) *trans*- and (b) *cis*-coordination of the carboxyl groups in the complex $\text{Cu}(d\text{-T})_2$

however, be expected to result in a stereoselectively favoured formation of the *dl*-complex in the *dl*-tartrate system. In the monotartrate complex the hydroxyl oxygen of the non-coordinated half of the tartrate ion has a position that makes an apical interaction possible either directly or via a hydrogen bond to a coordinated water molecule. When a second tartrate ion is coordinated in the *trans*-position in a *dd*-complex, this interaction would be disturbed or there would even set in a weak repulsion between the non-chelated halves of the tartrate ions. However, these effects should be weak as no structurally caused selectivity is observed in the formation of the CuT_2 complexes in the *dl*-system, but they could be strong enough to change the conformation of the chelate rings and either strengthen the circular dichroism in the first or weaken it in the second complex. Observations compatible with these ideas have been reported from studies of the circular dichroism of complexes between copper and suitably substituted amino acids.³⁷⁻⁴⁰

An interaction between the non-chelated tartrate halves would alternatively promote a small twist of the chelate rings out of the coordination plane inducing a configurational contribution to the circular dichroism.

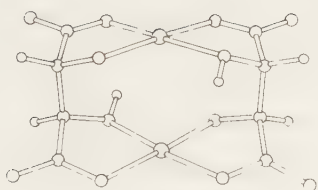
The larger values of the stability constants of the mononuclear copper *meso*-tartrate complexes as well as the greater basicity of the *meso*-tartrate ion may be taken as a demonstration of the

conformational differences between *meso*-tartrates and *d*- or *dl*-tartrates found in the solid phase. As mentioned in the introductory presentation of tartrate ions, the adjacent placing of the carboxylate groups would imply repulsive forces between the negatively charged groups. This conformation would, however, be preferred as any other conformation leads to short oxygen-oxygen contacts. Irrespective of what conformation the free *meso*-tartrate ion may take in the solution the coordination of a positive ion to the *meso*-tartrate ion in the mentioned conformation would lead to the release of repulsive energy and thus increase the total release of energy involved in the coordination. When a second positive ion is coordinated to the remaining carboxyl group the repulsive energy would, however, be practically exhausted. The observed equilibrium constants (reactions 1-6 in table 3) are in line with this picture.

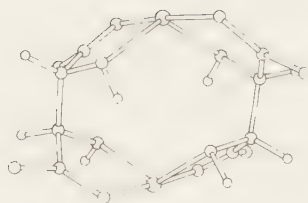
Binuclear complexes

The strength of the binuclear *d*- and *dl*-tartrate complexes indicates that the tartrate ion in these complexes makes full use of its chelate forming ability, *i.e.* each ion gives rise to two chelate rings. The tartrate-bridged dimers mentioned in the introduction are examples of structures with such a complete formation of chelates. These dimeric units are characterized by the two metal ions being bridged together by two tartrate ions and each tartrate ion forming a chelate ring with each metal ion. However, the coordination geometry around the metal ions varies as does the relative stability of *dd*- and *dl*-isomers.⁸

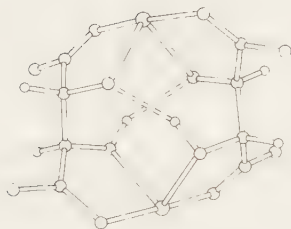
The stabilities of isomers of different combinations of *d*-, *l*-, and *meso*-tartrate ions have been discussed by Tapscott⁴¹ with consideration to the effects on the geometry of the tartrate ion. These effects are quantified by two parameters - one of them is the conformation angle of the tartrate ligand and the other a "strain angle" accounting for the strain introduced in the central carbon-carbon bond. From that study it appears that if the geometry of the tartrate ligand is considered only, a certain coordination geometry is preferred for a given combination of tartrate ions. Then the tetragonal coordination is



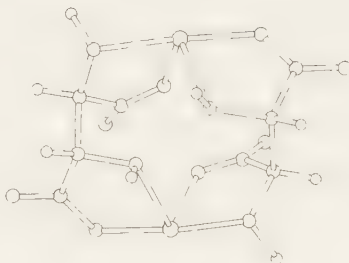
(a)



(b)



(c)



(d)

Fig. 4. Idealized geometries of tartrate-bridged binuclear complexes; (a) tetragonal geometry (*dl*-complex), (b) trigonal bipyramidal geometry (*dd*-complex), (c) octahedral geometry (*dd*-complex) and (d) octahedral geometry (*meso, meso*-complex).

most favourable for a *dl*-dimer (fig. 4a), while for the *dd*- or *ll*-dimers the chelate rings should be rotated about 80° from a joint plane i.e. a trigonal bipyramidal (fig. 4b) or an octahedral (fig. 4c) coordination geometry should be preferred. For the *meso-meso* combination (fig. 4d) the octahedral geometry is superior. The variation of the conformational energy of the bridging tartrate ions in various dimers as a function of the coordination geometry has been calculated by Tapscott *et al.*⁴² and is shown in fig. 5.

The combination of the geometrical factors of the tartrate ion and the coordination geometry preferred by the metal ion would determine the relative stabilities of different tartrate-bridged isomers.^{8, 41} A survey⁸ of examined structures shows this united

action of structure determining factors. The *dl*-isomer of the alkaline oxovanadium(IV) tartrate is more stable than the *dd*-isomer. This is in accordance with a tetragonal square pyramidal coordination geometry⁴³ of the oxovanadium(IV) ion. The *dd*-dimer shows a distortion towards a trigonal bipyramidal coordination. The alkaline copper *dl*-tartrate is built up from *dl*-dimers which, as expected, have a tetragonal coordination⁴⁴ geometry while it has not been possible to prepare the corresponding *d*-tartrate dimer. On the other hand, in the unhydrolyzed copper *d*-tartrate, $\text{Cu C}_4\text{H}_4\text{O}_6 \cdot 3 \text{ H}_2\text{O}$, a dimeric unit with an octahedral arrangement of the chelate rings is found.¹⁴ All of the examined structures of antimony(III) tartrate - *d*- as well as *dl*-tartrates - contain *dd*- (or *ll*-) dimers which is compatible with the fact that antimony(III) very often prefers a trigonal bipyramidal geometry.⁴³ The examples show that in these cases the choice between *dl*- and enantiomeric *dd*- and *ll*-dimers in *dl*-tartrates is governed by the possibility to give the metal ion a convenient coordination geometry.

The results of paper III show that the complexes $\text{Cu}_2(\text{d-T})_2$ and $\text{Cu}_2(\text{l-T})_2$ are stereospecifically formed in acid copper *dl*-tartrate solutions. Kinetic measurements on nickel *dl*-tartrate solutions¹³ have shown that an analogous behaviour is valid for the Ni_2T_2 -complex. In view of the disposition towards a square planar coordination of the nickel(II) and copper(II) ions, the above consideration on isomer stabilities would imply that the *dl*-dimer should be favoured. However, in a tetragonal *dl*-dimer with tartrate ions retaining the hydroxyl protons there would be an unsymmetrical distribution of charges around the metal ion as the coordinated carboxyl oxygens take a *cis*-position. The stereospecific formation of *dd*- and *ll*-dimers in these acid *dl*-tartrate solutions may be explained by the fact that these dimers make it possible to take up a *trans*-position for the negatively charged donor oxygens. The formation of increasing though uncertain amounts of *dl*-complexes when one or two hydroxyl protons are released implies that the coordination of deprotonated hydroxyl oxygens may increasingly balance the repulsion of *cis*-positioned carboxyl oxygens. When all the protons are released there will probably be a stereospecific formation of *dl*-dimers.^{7, 44}

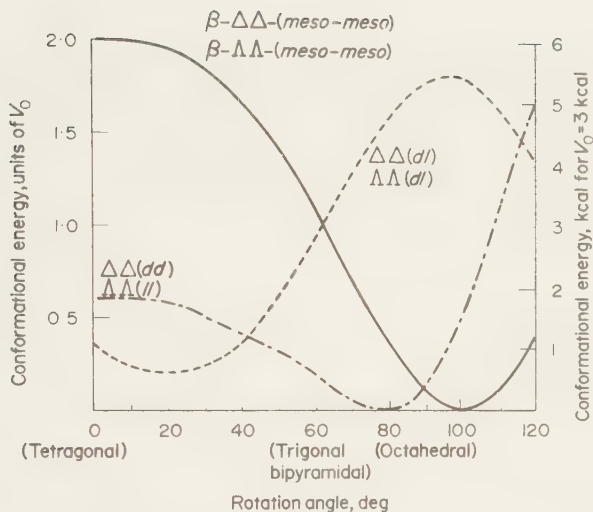


Fig. 5. Calculated conformational energies of the two tartrate bridges in the *dd*-, *ll*-, *dl*- and *meso,meso*-isomers of binuclear tartrate complexes as a function of the coordination geometry. (Reproduced by permission from ref. 41.)

Hypotheses on the actual coordination geometry of complexes in solution are of course uncertain. The calculations by Tapscott⁴¹ show that the strain in the central carbon-carbon bond of the tartrate ligand in a *dd*-dimer is small no matter whether the geometry is tetragonal or octahedral. With a tetragonal geometry, however, the conformation of the tartrate ion will be less favourable. The difference of conformational energy (from fig. 5) between the tetragonal geometry and the geometry most advantageous from the conformational point of view - with the angle between the planes of the chelate rings equal to about 100° - is certainly moderate, about 7 kJ per mol of dimer but would make a perfect tetragonal coordination geometry of the *dd*-dimer unlikely. However, geometries ranging from a distorted tetragonal to an octahedral one could be conceived.

The structure of $\text{Cu } d\text{-C}_4\text{H}_4\text{O}_6$ is the single examined structure of an unhydrolyzed metal tartrate in which dimers can be distinguished. In the dimeric units of this structure planar chelate rings are arranged in an octahedral coordination with an

almost perfect right angle between each other. The two positions not engaged by the chelate rings take a water molecule and a carboxyl oxygen from an adjacent dimeric unit. The fact that this geometry is preferred could well be caused by properties of the crystal structure as a whole and may not necessarily mean that this coordination geometry is adopted by the *dd*-dimers in the solution.

The large difference between the CD-spectra of the *dd*-dimers Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$ on the one hand and $\text{Cu}_2\text{T}_2\text{H}_{-2}$ on the other makes it probable that there are considerable structural differences between these complexes, and it could be suggested that these differences consist in changes of the coordination geometry. The tendency of formation of hydrogen bonds between opposite hydroxyl oxygens in an octahedral dimer should be most pronounced if each pair of hydroxyl groups has lost one proton as in the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$. Let us suppose that the hydrogen bonds contribute to stabilize an octahedral geometry of the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$. If the similarity of the CD-spectra of Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$ is taken as an indication that these complexes have almost the same coordination geometry, this would mean that the loss of only one proton does not change the geometry very much. It would then be concluded that the hydrogen bonds mentioned are absent in Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$, which would be equivalent to the assumption of a wide angle between the chelate rings. The coordination geometry of Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$ would thus approach a tetragonal coordination more or less distorted towards a square pyramid or trigonal bipyramid. At the same time it should be noted that such a change of geometry would be accompanied by a change of the conformation of the chelate rings.

In a tartrate-bridged dimer of the sort described there are different sources of dissymmetry that can be conceived to induce rotational strength in the ligand field band. In addition to the dissymmetry of the chelate ring including the asymmetric carbon atom configuration dissymmetry is conferred upon the *dd*-(Δ) or *ll*-dimers (Λ) as soon as the chelate rings are skewed in relation to each other. In such circumstances and lacking a comprehensive material for comparison it is difficult to make

definite conclusions on the structure of the binuclear complexes from CD-spectra. However, some features can be interpreted in a manner compatible with the related picture.

The crystal structure of copper *d*-tartrate trihydrate¹⁴, $\text{CuT} \cdot 3\text{H}_2\text{O}$, is the only piece of information on the structures of copper *d*-tartrates. The attempt in paper I to use this information and relate the CD-spectra of $\text{CuT} \cdot 3\text{H}_2\text{O}$ and the dehydrated tartrate, CuT, dispersed in KBr-discs to the CD-spectra of the binuclear complexes is of course tentative and subject to the uncertainty that is inherent in the measurement of circular dichroism of inhomogeneous phases. The measured dichroism of $\text{CuT} \cdot 3\text{H}_2\text{O}$ is weak and occurs mainly in the shorter wavelength range of the ligand field band. The dehydration of the trihydrate results in an obvious increase of the circular dichroism and at the same time a shift towards longer wavelengths. In the structure of $\text{CuT} \cdot 3\text{H}_2\text{O}$ one of the octahedral coordination positions is occupied by a water molecule. The structural changes that are associated with the loss of this water molecule are not known but it is possible that the resulting vacancy is compensated for by the change of the coordination geometry into a state with a larger angle between the planes of the chelate rings. If so this change is similar to the one that is supposed to occur when the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$ takes up one or two protons. We also observe that this latter process is accompanied by a change of the CD-spectra similar to the change occurring when $\text{CuT} \cdot 3\text{H}_2\text{O}$ is dehydrated.

The supposed modification of the structures when $\text{Cu}_2\text{T}_2\text{H}_{-2}$ takes up protons or $\text{CuT} \cdot 3\text{H}_2\text{O}$ loses its water implies a change from a state of a dissymmetry mainly caused by a dissymmetric configuration to a state of an increased element of dissymmetric contribution from puckered chelate rings. In paper I it is supposed that the observed wavelength shift of the circular dichroism is caused by different transitions being active in the two cases. An alternative explanation would be that the whole ligand field band is shifted because of a change of the strength of the ligand field that would be associated with the change of coordination geometry.

Two *meso*-tartrate ions can be combined together with two metal ions in several different ways in order to create a tartrate-bridged dimer. The analysis by Tapscott⁴¹ shows, however, that only two of them fulfil the demands of conformation and absence of strain in the tartrate ion *viz.* the octahedral (and enantiometric) $\Delta\Delta$ - and $\Lambda\Lambda$ -dimers in which the two asymmetric carbon atoms of each chelate ring at one and the same metal ion have opposite configurations. However, *meso,meso*-dimers are rare. No crystal structures containing the *meso,meso*-dimer are reported. The crystal structure of copper *meso*-tartrate trihydrate exhibits a chain structure.¹⁴ There are, however, a couple of chromium tartrate complexes⁴⁵ to which the *meso,meso*-dimeric structure has been attributed for reasons based on spectroscopic investigations.

The lower tendency of dimerization in the copper *meso*-tartrate system compared to the *d*- and *dl*-systems can be taken as a sign of the slight disposition of forming *meso*-tartrate-bridged dimers. Though the octahedral *meso,meso*-dimer is compatible with the demands of the individual tartrate ion, a dimer of this kind will contain rather short contacts either between opposed hydroxyl groups or between opposed carboxyl groups. Moreover, the carboxyl oxygens are *cis*-coordinated, which for the same reasons as in the case of the *dl*-dimer is supposed to be unfavourable as long as the hydroxyl protons are retained.

Polynuclear complexes

Several complexes containing more than two copper ions are reported in the papers under consideration in this work. All of them have in common that the ratio Cu/T is greater than one no matter whether they are formed in solutions with excess of copper or excess of tartrate. This fact as well as the very tendency to form polynuclear complexes is to be associated with the occurrence of several donor oxygens of the tartrate ion. As soon as the number of copper ions exceeds the number of tartrate ions by more than one, the complexes will necessarily contain other kinds of coordination than the five-membered chelate ring that is characteristic for α -hydroxocarboxylic acids. The poly-

merisation takes place at the same time as protons are released and it seems reasonable that deprotonated hydroxyl oxygens of the tartrate ions promote the polymerisation by acting as bridges between two copper ions. Such a bridging is demonstrated in the proposed structure of the complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$.

There are of course many possibilities to combine eight copper and six tartrate ions in order to produce a structure for $\text{Cu}_8\text{T}_6\text{H}_{-10}$. It should probably also be possible to find more than one structure that would describe the X-ray data of paper IV in a satisfactory way. There is no piece of evidence that alone is sufficient for a statement that the structure contains tartrate-bridged dimers. However, the comparison of CD-spectra, the interpretation of the potentiometric measurements as well as the appearance of a peak in the radial distribution function at the proper distance 5.25 Å indicate the occurrence of a dimer of the octahedral geometry present in $\text{Cu d-C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$.

The complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$ is formed in neutralized solutions with a wide range of tartrate concentrations from equal amounts of copper and tartrate to a considerable excess of tartrate. The quantitative formation of the complex under these conditions indicates a compact structure that gives limited possibilities for further coordination of tartrate ions. This requirement is met by the proposed structure, which also gives an obvious explanation to the number of released protons.

The polynuclear complexes with four tartrate ions that are formed in solutions with excess of copper, are able to accommodate a varying number of copper ions. A rather open structure would be suggested. The positive sign of the dominant circular dichroism band makes it probable that these complexes do not contain the dimers with Δ -configuration. A change to the Λ -configuration or a change of the conformation of the kind outlined in paper II would favour the formation of an open structure.

Tris-tartrato chromium(III) complexes

The characterization of the deprotonated tris-tartrato chromium(III) complex, $\text{Cr}(\text{d-TH}_{-1})_3$, is founded on the observation that the specific circular dichroism of chromium tartrate solutions with a substantial excess of tartrate is independent of the tartrate and chromium concentrations as well as pH when three hydroxide ions per chromium ion have been consumed. The complex should then be coordinatively saturated, which together with the large dissymmetry factor, $\Delta\epsilon/\epsilon$, is a strong indication of the formation of a tris-chelate. This will in turn imply that the released protons in this case must derive from the hydroxyl groups of the tartrate ions, i.e. one proton from each coordinated hydroxyl group.

The large circular dichroism of the $\text{Cr}(\text{TH}_{-1})_3$ complex indicates an almost complete selection of one configuration of the tris-chelate complex. According to the empirical rule for the rotational strength of trigonal d^3, d^6 complexes⁴⁶ this complex with positive circular dichroism in the ${}^4\text{T}_{2g} + {}^4\text{A}_{2g}$ transition should have the Λ -configuration, a configuration which can also be made probable from a comparison of structural models of the different tris-tartrate isomers (fig. 3 of paper VI). It turns out that the Λ -forms can be stabilized by internal hydrogen bonds.

When pH is lowered the circular dichroism is drastically decreased and the stereospecificity nullified as soon as one proton per chromium ion is returned, and at $\text{pH} \approx 6$ the sign of the circular dichroism is shifted. The complex formation can no longer be satisfactorily described with merely tris-tartrate complexes. The increase of the CD-minimum when the tartrate concentration is decreased at constant pH in the weakly acid solution indicates that the maximum degree of chelation is passed when the tartrate concentration has reached one $\text{mol}\cdot\text{dm}^{-3}$ and that a fourth tartrate ligand has been introduced. The negative circular dichroism shows that the Λ -configuration now is preferred but the degree of stereoselectivity cannot be estimated as the complex composition of the solutions is not known.

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APPENDIX

Application of the potentiometrically determined set of complexes to CD-data.

Among the complexes that are introduced for the description of the potentiometric data of paper III there is one complex, *viz.* $\text{Cu}_2\text{T}_2\text{H}_{-1}$ that is not used in the calculations on the CD-data of paper I but that should obviously not be neglected in these calculations. On the other hand, the complex Cu_2T_3 was supposed to take an important part in the model used for the description of the CD-data but the existence of this complex cannot be statistically ascertained from the potentiometric data. Thus it was interesting to find out if the CD-data could be better described by a set of complexes taken from the potentiometric study.

The complexes from paper III that should be of importance in the concentration ranges valid for the CD-data are the following, CuT , CuT_2 , Cu_2T_2 , $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and $\text{Cu}_2\text{T}_2\text{H}_{-2}$. The mononuclear complexes can be estimated to reach at the most about 20% of the total copper concentration.

Preliminary calculations show that the changed model does not give a more plausible CD-spectrum of CuT_2 than was possible in the original calculations in paper I. An estimation of the composition of the solution used in paper I for the separate determination of the CD-spectrum of CuT_2 shows that this solution - as stated in paper I - is obviously dominated by the complex CuT_2 , but the presence of a few percent of binuclear complexes characterized by their strong circular dichroism gives a considerable contribution to the total circular dichroism. A small uncertainty in the spectra and the amounts of the binuclear complexes present is combined with a large uncertainty in the spectrum of CuT_2 . However, the circular dichroism of CuT_2 should not be more negative than that recorded for a solution dominated by the complex. With the opportunity of using a more sensitive CD-instrument (JASCO J-41 dichrograph) the CD-spectra of such solutions were repeated. Such a spectrum is reproduced

in fig. 1 ($C_M = 10^{-4}$ M, $C_T = 0.1$ M, pH = 4.5, and $I = 1$ M (NaClO₄)). It is observed that the circular dichroism is even weaker than that recorded earlier. Accordingly, the circular dichroism of CuT₂ consists of a very small negative band which perhaps may take even positive values in the wavelength region about 800 nm. For the reasons mentioned above it seems, however, impossible to obtain a reliable CD-spectrum of CuT₂ as the circular dichroism of solutions with still lower copper concentration cannot be satisfactorily measured with the present instrumentation. In the continued calculations the circular dichroism of CuT₂ is set equal to zero.

The two sets of complexes, differing from each other by the exchange of Cu₂T₃ of one set against Cu₂T₂H₋₁ in the other, were tested without other assumptions than those concerning the spectrum of CuT₂. The calculations were performed as earlier by the use of the Letagrop program SPEFO. CD-data deriving from three wavelengths - the same as in paper I - and from solutions with $C_T \leq 100$ mM were used. It turned out that the model containing the complex Cu₂T₂H₋₁ gave a slightly better description of data (the sum of least-squares is lowered about 25%). It is further observed that the CD-spectrum of CuT is now about the same size as that presented in paper II. The stability constants obtained,

$$\begin{aligned}\beta_{110} &= (9 \pm 5) \cdot 10^2 \text{ M}^{-1}; & \beta_{120} &= (3.3 \pm 1.9) \cdot 10^4 \text{ M}^{-2}; \\ \beta_{220} &= (1.1 \pm 0.9) \cdot 10^9 \text{ M}^{-3}; & \beta_{22-1} &= (4 \pm 4) \cdot 10^4 \text{ M}^{-2}; \\ \beta_{22-2} &= (0.8 \pm 0.8) \cdot \text{M}^{-1}; & & (\text{errors equal to three } \sigma).\end{aligned}$$

are of the same order of magnitude as those determined from potentiometric data though about two times greater and show low statistical significance. The CD-measurements are performed at 20°C and the potentiometric ones at 25°C. The difference between the constants is much greater than would be expected from the temperature difference and is probably a consequence of the great stability of the binuclear complexes, the stability constants of which approach the magnitude above which it becomes difficult to obtain significant stability constants from this

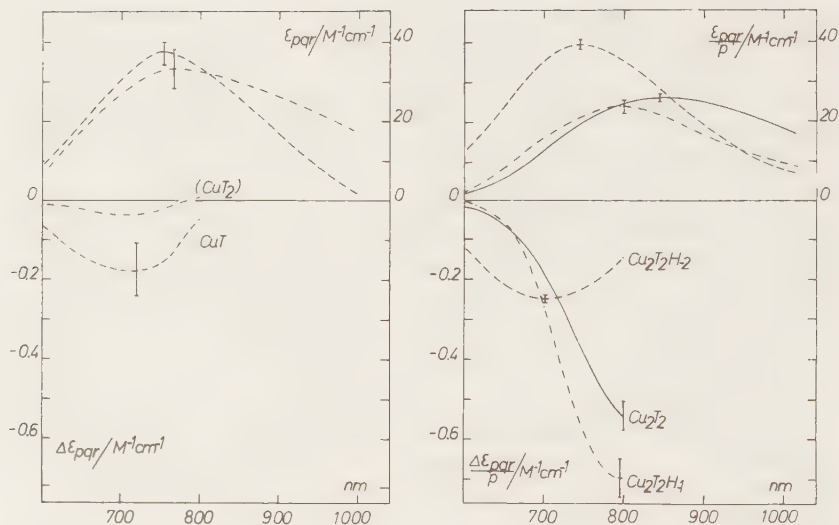


Fig. 1. Absorption and circular dichroism spectra of copper *d*-tartrate complexes. The spectra are calculated from the CD-data of paper I but with the use of a set of complexes which together with their stability constants are taken from the potentiometric measurements of paper III. The CD-spectrum ascribed to CuT_2 has been taken directly from a spectrum recorded for a solution dominated by that complex. The inserted bars represent three standard deviations.

kind of data. However, CD-spectra calculated from these constants do not differ very much from corresponding spectra presented in fig. 1 which are calculated by the use of the potentiometric constants.

Even if an exchange of Cu_2T_3 against $\text{Cu}_2\text{T}_2\text{H}_{-1}$ improves the fitting of the data, the existence of Cu_2T_3 cannot be excluded. It is evident that the constant of the complex presented in paper I is far too large. A calculation with both $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and Cu_2T_3 present gives however stability constants with hardly any statistical significance at all.

The spectra of fig. 1 are calculated by the use of potentiometric constants and CD-data with $C_T \leq 100$ mM. For the CD-spectrum of CuT , however, data with $C_T \leq 25$ mM are used rep-

representing a region in which this sparingly occurring complex has its primary existence (max. 17%). If all the data are used a spectrum of the complex with accordant magnitude and wavelength of the minimum is obtained but which is less reliable in the wavelength region just below 800 nm. The mentioned difference in temperature would introduce some errors in the calculated spectra but it is supposed that those errors are fairly small and will not affect the general features of the particular spectra.

A comparison of the spectra of fig. 1 and those of fig. 3 in paper I shows that the introduction of $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and the exclusion of Cu_2T_3 change the spectra of the complexes Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-2}$ presented in paper I very little but that a more plausible magnitude of the CD-minimum of CuT is obtained.

The CD-spectrum of $\text{Cu}_2\text{T}_2\text{H}_{-1}$ is very similar to that calculated for Cu_2T_3 in paper I. Moreover the region of occurrence of the two complexes should roughly be the same. These two facts provide an explanation as to why the CD-data could be satisfactorily described without the use of the complex $\text{Cu}_2\text{T}_2\text{H}_{-1}$ in paper I.

